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ORIGINALPAPER

Diesel Soot Catalyzes the Selective Catalytic Reduction of NO_x with NH_3

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Abstract The catalytic activity of soot samples for the selective catalytic reduction (SCR) of NO_x with NH_3 was investigated in dependence of the NO_2, NO and NH_3 concentration in the temperature range between 200 and 350 °C. The highest NO_x reduction of up to 25 % was measured in the presence of both NO_2 and NO at a GHSV of 35,000 h^{-1}. Decreasing space velocities resulted in an increase of the SCR activity. In the absence of NO_2, NO_x reduction was not observed. Carbon oxidation and SCR reaction occurred in parallel due to the presence of NO_2 and O_2, but hardly influenced each other, which suggested that in the NO_x reduction on soot most probably physisorbed species were involved. The observed stoichiometries indicated the action of the *fast SCR* reaction in the presence of NO and the *NO_2 SCR* reaction in the absence of NO, while the observed gas phase and surface species pointed at reaction steps similar to those on classical SCR catalysts.

Keywords Selective catalytic reduction (SCR) · Diesel soot · Soot · Fast SCR · NO_2 SCR

1 Introduction

The selective catalytic reduction (SCR) of the nitrogen oxides with ammonia as reducing agent has become the state-of-the-art technology for heavy-duty diesel engines and also for passenger cars [1, 2]. The currently applied catalysts for the SCR process are either vanadia-based catalysts (mostly $V_2O_5/WO_3{-}TiO_2$) or metal-exchanged zeolites (metals: Fe, Cu) [2]. The toxic and corrosive NH_3, which is required in this process, is stored in form of an aqueous solution of the harmless NH_3 precursor compound urea in an extra tank in the vehicle. In dependence on the actual amount of NO_x in the exhaust gas the urea solution is injected into the exhaust stream, where it thermolyzes and hydrolyzes to NH_3 and CO_2.

Before SCR was introduced to diesel vehicles, it had already been used for the reduction of NO_x in stationary applications for several decades [3, 4]. For special low temperature applications at 100–150 °C, activated carbon catalysts were developed for the reduction of NO at space velocities of approx. 2,000 h^{-1} in the 1970s and 1980s [5–14]. The up to 80 % conversion reached with these catalysts strongly depends on the carbon type and pre-treatment [8]. Whereas many parameters remain unclear, the amount of acidic surface functional groups on the carbon surface were shown to be important for the adsorption of NH_3 [15–18] and nitrogen embedded in the carbon structure increased the activity [7, 19, 20].

The oxidation of NO with oxygen to NO_2 is assumed to be a prerequisite step for the SCR reaction on soot in presence of NO [5, 20, 21], which takes place at an oxygen-containing surface functional group consisting of an active carbon carrying chemisorbed oxygen [20]. NO adsorbs well on these complexes leading to the formation of NO_2 [20]. It is assumed that NO_2 and NO yield N_2O_3 [5, 14], which reacts with NH_3 and water to ammonium nitrite (NH_4NO_2). The decomposition of NH_4NO_2 leads directly to nitrogen and water. Based on these reaction steps, an overall reaction equation was formulated, showing the 1:1 NO/NH_3 ratio of the *standard SCR* reaction:

$$NO + O_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O$$

Tighter future emission limits for diesel vehicles will necessitate the application of both diesel particulate filter

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(DPF) and SCR system in the same vehicle. In order to keep exhaust gas aftertreatment compact and simple, new concepts suggest combining both functions in one aftertreatment device, i.e. DPF and SCR catalyst could be placed in the same housing or the DPF could be coated with an SCR catalyst. Consequently, soot, NH_3 and NO_x are present in the same reaction device. It is obvious that the chemistry in such combined DPF-SCR systems has to be understood for a proper reaction design and before such systems can be brought to the market. The above mentioned studies provide valuable information about a possible SCR effect over soot. However, the temperatures were much lower and the space velocities were more than ten times lower, which requires revisiting the SCR reaction over soot under the conditions relevant for diesel exhaust gas aftertreatment.

2 Experimental

2.1 Catalytic Tests

The SCR tests over diesel soot were performed under isothermal conditions at temperatures between 200 and 350 °C in a heated tubular quartz reactor (length: 650 mm, ID: 49 mm). For the gas analysis the reactor was connected to a FTIR spectrometer (Nicolet Nexus 600) via a heated quartz glass tube. The gas measuring cell had a path length of 2 m and each spectrum was the average of 8 scans at a resolution of 0.5 cm^{-1}. The soot samples were loaded on 400 cpsi cordierite monoliths by dip coating into a dispersion of soot and isopropyl alcohol (IPA). The loaded monoliths were placed in a sample holder and fitted into the reactor with a ceramic fiber mat to avoid any bypass. NO, NO_2, NH_3, O_2 and N_2 were provided by a gas mixing unit consisting of six mass flow controllers (Brooks 5850S). Water was generated by controlled hydrogen oxidation over a Pt catalyst (2 % Pt on SiO_2). The base feed gas, which was used for all experiments, consisted of 10 % oxygen and 5 % water with nitrogen as balance at a total flow of 550 or 275 L/h at STP. By variation of both, the total flow and the monoliths size, gas hourly space velocities (GHSV) of 3,000, 9,000, 17,000, 35,000 and 70,000 h^{-1} were realized. Prior to the actual catalytic tests the soot samples were activated for 25 min with 250 ppm NO_2 + 250 ppm NH_3 in the base feed gas. This activation became necessary as preliminary experiments showed that the samples went through a significant activation phase, which reduced the reproducibility. For each temperature a new soot-coated monolith was used. Each experimental series was repeated three to five times and terminated at 50–60 % soot conversion in order to avoid interference by soot limitation.

Most experiments were performed with the synthetic soot Printex U from Evonik, supplemented with a limited number of experiments with real diesel soot from heavy-duty diesel engines, complying with old Euro 0 and recent Euro V emission limits. In addition a mixed soot sample collected from several heavy-duty diesel engines was used. The BET surface area of Printex U was 103 m^2/g, of the Euro V soot sample 110 m^2/g, of the Euro 0 soot sample 132 m^2/g and of the mixed soot sample 145 m^2/g. Printex U did not contain metals above the detection limits of an ICP-OES analysis. In the Euro V, Euro 0 and the mixed soot sample about 1 % Ca, 1 % Fe beside some Zn, Mg, Na and K could be found (for details refer to [22, 23]). TEM measurements of Printex U and the Euro V soot showed hardly any difference in size and structure of the primary particles between the different samples. However, the Euro V sample might be slightly more amorphous than Printex U.

3 Results and Discussion

3.1 SCR Reaction over Printex U in the Presence of NO and NH_3

In a preliminary experiment we tested Printex U for its SCR activity under conditions similar to previous studies in the 1980s on activated carbon [5–14, 24]. However, at a GHSV of 3,000 h^{-1} no NO_x reduction activity was observed for Printex U with NH_3 when NO_x was only NO. In contrast, considerable NO_x reduction could be observed in the presence of NO_2. Based on this observation NO_2 was always added to the feed and only the concentrations of NO, NO_2 and NH_3 were varied.

Figure 1 shows the NO_x reduction rates over Printex U at temperatures between 200 and 350 °C for varying NH_3 feed gas concentrations. Beside the NO_x reduction, the measured stoichiometry, i.e. the ratio of consumed NH_3 and consumed NO_x is plotted on the secondary *y*-axis. Under the experimental conditions NO_x reduction increased with temperature and reached a plateau up to 36 % at 300 °C. Increasing NH_3 concentration also resulted in higher NO_x reduction rates. It should be noted that up to 80 % NO_x conversion was reached when the space velocity was reduced to 3,000 h^{-1} (results not shown). Regarding the stoichiometric ratios in Fig. 1, between 250 and 300 °C stoichiometric ratios of 1.25–1.50 were found indicating within the measurement error the *NO_2 SCR* reaction with a theoretical stoichiometry of 1.33 (NH_3:NO_2 = 4:3 = 1.33):

$$4NH_3 + 3NO_2 \longrightarrow 7/2N_2 + 6H_2O$$

At 200 °C, the conversions were to low to reliably determine the stoichiometric ratio. The increasing ratios at

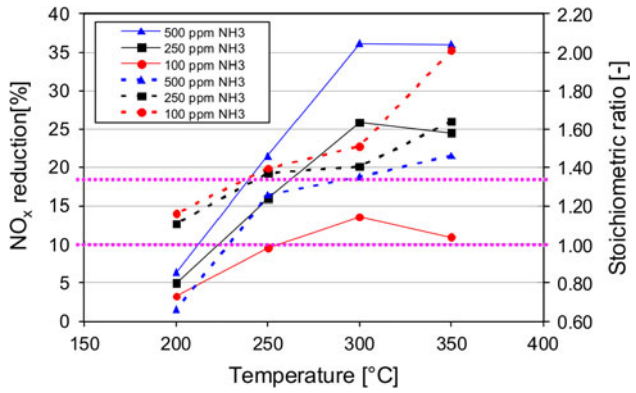

Fig. 1 NO_x reduction and measured stoichiometric ratios ($=NH_{3,consumed}/NO_{x,consumed}$) over Printex U in dependence of the NH_3 concentration at a GHSV of 35,000 h^{-1}. Base feed + 250 ppm NO_2 + variable NH_3 concentrations. *Solid lines* NO_x reduction [%]; *dotted lines* measured stoichiometric ratios; *purple dotted lines* calculated stoichiometric ratios of the *fast SCR* and *NO_2 SCR* reaction

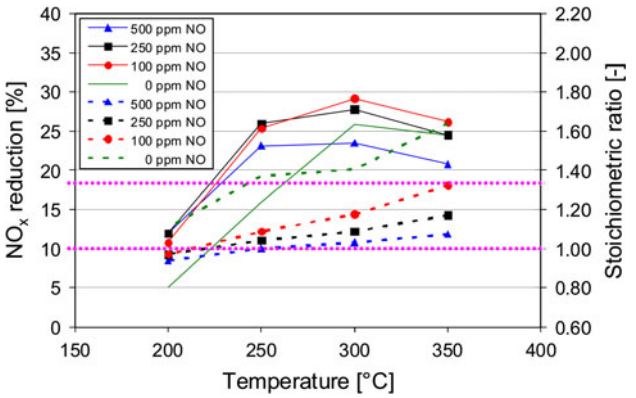

Fig. 2 NO_x reduction and measured stoichiometric ratios ($=NH_{3,consumed}/NO_{x,consumed}$) over Printex U in dependence of the NO concentration at a GHSV of 35,000 h^{-1}. Base feed + 250 ppm NO_2 + 250 ppm NH_3 + variable NO concentrations. *Solid lines* NO_x reduction [%]; *dotted lines* measured stoichiometric ratios; *purple dotted lines* stoichiometry of the *fast SCR* and *NO_2 SCR* reaction

350 °C are caused by the oxidation of NH_3 to N_2 and to a small extent to NO as well as the formation of HNCO and HCN from side reactions of NH_3 with carboxylic surface functional groups.

The almost constant NO_x reduction above 300 °C is due to a limitation of the reaction by NO_2. NH_3 oxidation is also the reason for the generally higher stoichiometric ratios when the NH_3 feed gas concentration was increased.

When NO was added in varying concentrations to constant amounts of NO_2 and NH_3 the NO_x reduction rate further increased, as observable in Fig. 2 when comparing the green NO_2/NH_3 reference line with the black, red and blue lines, which represent the $NO/NO_2/NH_3$ mixtures. However, at 300 °C or higher this advantage of the NO/NO_2 mixture is less pronounced or the NO_x reduction rates even decline below the rates of the NO_2/NH_3 reference experiment. The observed stoichiometric ratios decreased with increasing NO concentrations, reaching values around 1 for 250 and 500 ppm NO, which are in accordance with the stoichiometry of the *fast SCR* reaction [NH_3:NO_x = 4/(2 + 2) = 1]:

$$4NH_3 + 2NO + 2NO_2 \longrightarrow 4N_2 + 6H_2O$$

The slightly higher stoichiometry for 100 ppm NO can be explained most likely with the occurrence of the *fast SCR* and *NO_2 SCR* reaction in parallel.

In the presence of 500 ppm NO, the observed stoichiometry indicated the occurrence of the rapid *fast SCR* reaction, but the NO_x reduction activity seemed to be higher for the NO_2/NH_3 reference experiment. In order to understand this effect, please keep in mind that NO_x reduction is a relative unit, i.e. although the NO_x reduction is nominally lower with NO in the feed gas the absolute amount of converted NO_x was higher when 500 ppm NO + 250 ppm NO_2 = 750 ppm NO_x were dosed compared to the reference case with only 250 ppm NO_2 = 250 ppm NO_x. In fact, a detailed analysis of the ongoing reactions, based on the balance of all reactants and products, clearly showed that an almost constant fraction of the NO_2 was consumed in all experiments for the oxidation of soot and the rest was either consumed in the *fast SCR* or the *NO_2 SCR* reaction. Since the *fast SCR* is more efficient than the *NO_2 SCR* reaction, the *fast SCR* reaction run into an NO_2 deficit and the remaining NO could not be converted in the SCR reaction as shown in the preliminary experiment.

3.2 $NO_2/NO/NH_3$ Reaction Network over Printex U

The relationship of NO_x reduction reactions and parallel occurring soot oxidation was investigated in detail. Variations of all parameters revealed that the *C*-oxidation rates, calculated on basis of the current amount of remaining carbon, were almost independent of the NO and NH_3 concentration in the feed gas. However, an increase of the NO_2 concentration led to an expected increase of the *C*-oxidation rate.

Figure 3 exemplarily shows the *C*-oxidation rates during the experiment in Fig. 1, which were hardly influenced by the varying NH_3 concentrations. The slightly lower oxidation rates at 250–300 °C for 0 and 100 ppm NH_3 in the feed gas compared to the other concentrations can be explained by the decomposition of nitrile and amide species, which are formed from the reaction of NH_3 with carboxylic functional groups, as reported in [25]. The decomposition products of these functional groups are HCN and HNCO, respectively, which were found in traces in our experiments. For details of the involved chemistry please refer to Ref. [22, 23].

The measured *C*-oxidation rates for different NH_3, NO and NO_2 concentrations showed only a minor influence of the SCR conditions on the soot oxidation. This suggested that nitrogen species involved in the SCR process did not affect the decomposition of surface functional groups responsible for the soot oxidation. It can be concluded that the NO_x surface species involved in the SCR reaction did not form strong bonds with the soot (e.g. surface nitrates and nitrites) and had a more physisorbed nature. Supplementing DRIFTS measurements (results not shown) proved that surface functional groups with chemical C–N and C–O bonds were indeed formed [26–29], but these groups were most probably only involved in soot oxidation and not in the SCR reaction.

Beside the above mentioned main gas components, HCN, HNCO, N_2O, HNO_3 and HONO (HNO_2) were detected in concentrations between <1 and 10 ppm during the investigation of the NO_x reduction over Printex U, which provided valuable information about the mechanisms of SCR reaction, soot oxidation and unselective side reactions. Whereas HCN and HNCO are decomposition products of nitrile and amide surface functional groups, formed upon reaction of NH_3 with carboxylic groups, HNO_3 and HONO (HNO_2) are typical intermediates of the *fast SCR* and *NO_2 SCR* reaction formed upon disproportionation of NO_2 on the carbon surface in the presence of water [30–32]:

$$2NO_2 + H_2O \rightarrow HNO_3 + HONO$$

Furthermore, HONO could be generated via hydrogen abstraction from the soot surface by NO_2 as shown in [33] and as it is known from partial oxidation of light organic molecules in the gas phase [34]. HNO_3 and HONO readily react in the presence of NH_3 to ammonium nitrate (NH_4NO_3) and ammonium nitrite (NH_4NO_2). These are

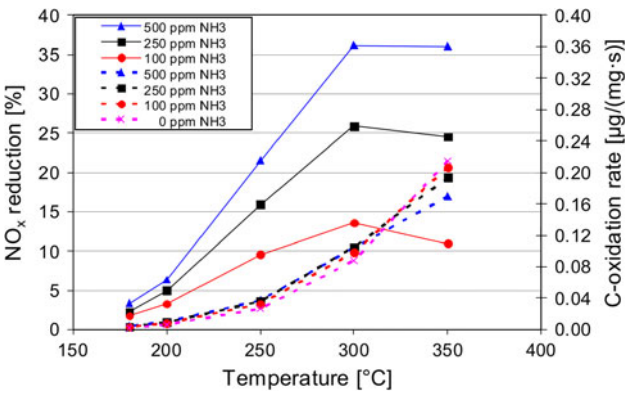

Fig. 3 NO_x reduction and *C*-oxidation rates of Printex U during the SCR measurements in dependence of the NH_3 concentration between 200 and 350 °C at a GHSV of 35,000 h^{-1}. Base feed + 250 ppm NO_2 + variable NH_3 concentrations. *Solid lines* NO_x reduction [%]; *dotted lines C*-oxidation rates

the same compounds as the well-known intermediates of the *fast SCR* and *NO_2 SCR* reaction over inorganic SCR catalysts. NH_4NO_2 is unstable above 60–70 °C and decomposes to N_2. NH_4NO_3 has to be reduced in case of the *fast SCR* reaction with NO to NH_4NO_2, which again decomposes to N_2, and in case of the *NO_2 SCR* reaction with NH_3 over several steps to the final SCR product N_2. Summing up all reaction steps lead to the overall stoichiometries of *fast SCR* and *NO_2 SCR* reaction, respectively.

Finally, also the formation of small amounts of N_2O can be easily explained with this reaction network. N_2O might be formed as result of the thermal decomposition of the intermediate NH_4NO_3 or from the oxidation of NH_3:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$
$$3NH_3 + 4NO_2 \rightarrow 3.5N_2O + 4.5H_2O$$

3.3 SCR Reaction over Diesel Soot in Comparison to Printex U

When selected experiments of the study with Printex U were repeated with the Euro 0, Euro V and mixed diesel soot sample, similar catalytic results were obtained, except the general SCR activity level, which was significantly reduced (Fig. 4). According to correlations in literature between general soot reactivity and surface acidity [9, 15, 16, 35–37], one reason for the high NO_x reduction rates over Printex U was most probably its high activity to form acidic surface functional groups on the carbon surface upon exposure to NO_2, which is supported by the observed evolution of higher amounts of HCN and HNCO from Printex U (results not shown). Since the organic carbon content of this soot (i.e. the tar-like soot components) was <1 % the elemental carbon fraction was most likely responsible for the formation of acidic surface functional groups.

The consumption of HNO_3 during SCR on soot according to the above described SCR chemistry was supported by the comparison of the diesel soot samples and Printex U. The diesel soot samples showing lower NO_x reduction evolved higher amounts of HNO_3, because it was not consumed in the further SCR process. In addition, higher amounts of HNO_3 evolved from the real diesel soot samples suggesting that the disproportionation of NO_2 to HNO_3 and HONO, which is a prerequisite for the occurrence of the SCR reaction, was most probably not the rate limiting reaction step. This also indicates that the adsorption properties for NH_3 were the critical factor for the SCR reaction over soot in analogy to inorganic SCR catalysts, for which surface acidity is decisive to adsorb NH_3 and consequently reach high activities. This significance of acidic surface functional groups for the adsorption of NH_3

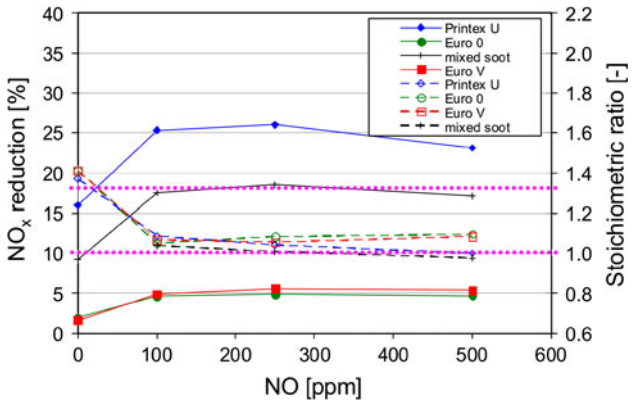

Fig. 4 NO_x reduction and measured stoichiometric ratios ($=NH_{3,consumed}/NO_{x,consumed}$) over Printex U, Euro 0, Euro V soot and the mixed soot sample in dependence of the NO concentration at 250 °C. GHSV: 35,000 h^{-1}. Base feed + 250 ppm NO_2 + 250 ppm NH_3 + variable NO concentrations. *Solid lines* NO_x reduction [%]; *dashed lines* measured stoichiometric ratios; *purple dotted lines* stoichiometric ratios of the *fast SCR* (=1) and *NO_2 SCR* (=1.33) reaction

due to acid–base-interaction [15–18, 38, 39] was confirmed by DRIFTS measurements (results not shown) showing NH_4^+ bands only in the presence of NO_2, which causes the formation of acidic carboxylic groups on the soot surface.

Considerable amounts of inorganic components have been found in the diesel soot samples by ICP-OES. Regarding the iron-content of approx. 1 % in all samples, the question arises if the soot activity might have been caused by this redox-active component. However, if this assumption is right significantly higher activities would have been expected for the real soot samples compared to the pure Printex U, whereas the opposite was found experimentally. It can be speculated if the alkali metals in the diesel soot samples might have led to the lower NO_x reduction activity due to their strong basicity, in accordance with findings of Ahmed et al. [40].

4 Conclusions

The investigations of the NO_x reduction by SCR with NH_3 showed that model and diesel soot samples were able to remove NO_x in model exhaust gases up to 25 % at 35,000 h^{-1}. The presence of NO_2 in the feed gas was a prerequisite for NO_x reductions, because NO_2 disproportionation was the initial step of the SCR process on soot. Depending on the presence or absence of NO, the *fast SCR* or the *NO_2 SCR* reaction pathway was followed, respectively, which was supported by the observed NH_3:NO_x consumptions, the reaction intermediates in the gas phase and the detected surface species.

The obtained results are important for future combined DPF-SCR systems, where urea (or rather NH_3) and NO_x are present together with soot, since significant NO_x reduction has to be expected in the presence of soot even at high space velocities characteristic for vehicle applications.

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